Solid State Chemistry
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Lecture – 03
Solid State Chemistry- Week 2 Lecture 1 Unit Cell

Welcome to week 2 of this course. In this week we will be talking about Unit Cells, Primitive and Conventional Unit Cells, then we will talk about lattices, Bravais Lattices and what a crystal is. So, in the first lecture of this week I will talk about the Unit Cell. So, we have week 2, lecture 1 which will be on the Unit Cell.

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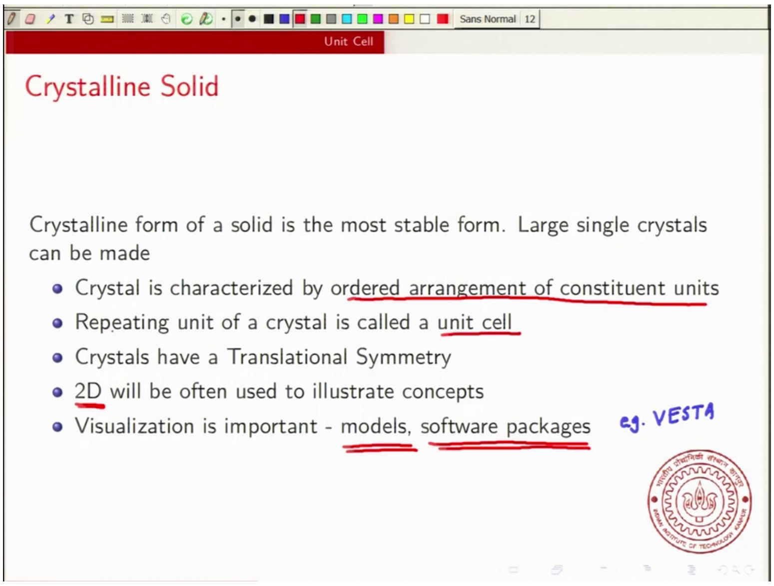

So, as we have already seen crystalline solid refers to a form of a solid in the most stable form, and as we know you can actually make very large single crystals, ok. And so, a crystal is characterized by an ordered arrangement of its constituent units, and the repeating unit of a crystal is called a unit cell, ok. So, the crystal is characterized by an ordered arrangement of constituent units. So, all these constituent units are arranged in some order and that repeating unit of the crystal is referred to as a unit cell, ok.

Now, since the crystals have a translational symmetry you can take the unit cell, you can take the unit cell and repeatedly by replicating it you can generate the entire crystal and we will illustrate this soon. So, the unit cell actually if it if you translate the unit cell repeatedly you will generate the entire crystal.

So, in this topic we will often need to have visual representations and sometimes we will be using two dimensional representations, to illustrate concepts, just because they are easier to draw, ok. But you should not stop at what is done in the class in the course, you should also look up various visualization tools. So, there are various like you can construct 3D models using fairly simple objects, you can construct like a ball and stick models, but there are also very nice software packages that will help you visualize some of these structures, ok. One very one particularly well-known software package is called VESTA, this is a freely available software package and it can you can really visualize crystal structures quite well that vesta, ok. So, I encourage all of you to look up some of these visualization software so that you can you can get a better understanding of crystalline solids, ok.

So, now, we will keep in mind that the repeating unit of the crystal is called a Unit Cell.

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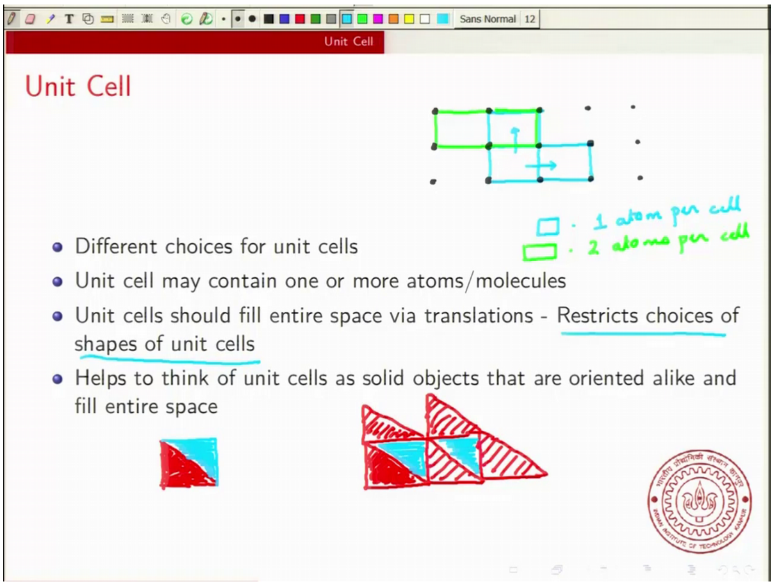

So, it turns out that there are different choices of for unit cells, and as I had said we will use an example of a 2D lattice, and we will just illustrate this. So, let us take a simple, for now I will just take a I will just take a rectangular 2D lattice.

So, if you have a rectangular 2D lattice something like this. Now, if I want to choose my unit cell I have I can choose either, either this unit as a repeating unit, ok. And notice that since crystals are translationally invariant, it will just emphasize the points of whatever, so these points are whatever the constituent units are, so they may be atoms they may be different units, ok, but these are the constituent units of the crystal.

So, suppose I have, suppose I choose this as my unit cell you can easily see that I can translate it, by taking it repeatedly I can generate the entire crystal. So, I take the same thing put it here, translate it; translate it means you shift the unit cell, ok. And you will get this and if you keep doing this you will generate you will be able to generate the entire crystal without any voids. So, we will soon see what it means by without any voids. But notice that I just translated it in these directions along the axis, ok. So, along these two axis you have translated, you translate it in these two directions. And by translating this unit cell you are generating more of the solid, and if you keep translating in all directions, if you keep translating multiple times you will generate the entire crystal, ok.

Now, as I said there can be different choices of unit cell. So, I will just show you another choice of unit cell, I think I think it is fairly obvious, ok. So, I could take this as my choice of unit cell, I could take this green rectangle, which actually consists of two of these, two of these blue rectangles as a choice of unit cell, and everything would follow I mean there is no you would still be able to translate the green rectangle in all directions and generate the entire crystal, ok.

So, in a sense there are many choices of unit cells, there are different choices. I will also mention this, but I will not illustrate this, you can also you know you know change the shapes and you know construct look at different objects also, ok. But we will just mention that there are different choices of unit cell and unit cell may contain one or more atoms or molecules. So, if these were individual atoms, then the blue square contains 4 atoms, but each atom is shared by 4 other cells, so effectively it contains each atom contributes quarter to each unit to the unit cell. So, the blue square contains only 1 atom per unit cell. So, this or blue rectangle, this contains 1 atom per unit cell per cell whereas, the green one as you can see contains 2 atoms per cell.

So, there are there is another very important restriction about the unit cell and I mentioned this, that the unit cells should fill the entire space via translations, and this actually restricts the choices of available shapes of unit cells, ok. And just to give you an idea in let us look at two dimensions again, ok. And let me consider a shape, which let us take a simple example, let us take a shape we are looking at two dimensions and let me take some shape that looks like this, ok.

So, can I have shape like this be a unit cell in 2D, ok? And the answer is no, because if you translate this shape, so clearly if you translate this shape, you will whichever direction you translate the shape, you will never be able to fill space. So, if you translate it you will be left with voids, ok. So, these are your cells. So, by translating these cells, you see that there are voids which I will show by this blue, with this blue color. So, these are voids in this cell. And you can clearly see that whatever you do, whichever way you translate it, whichever direction you translate it you will always end up with voids if you choose this as your starting point for the cell, ok.

Now, you could argue that if I take this light blue region which is which was the void, and I imagine that I actually take another cell, but I just turn it around, so if I take this if I take this cell, this cell and I just turn it around, I will get this blue cell. So, you could say that that these two units, this combination of these two units, one like this and one like this, this can fill space, ok.

So, I can take two in opposite orientations and use it to fill space, but that is not that is not sufficient to call only this red region or only this red region as a unit cell, ok. So, you might say that I can take the same red region and just turn it around and I will get the blue region, and then and then this combined red and blue region can actually fill space, ok. But these are two or these are an opposite orientations, ok. And what is important is that the unit cell should fill the entire space via translations, ok. So, these two the red and the blue have a rotational relation and you are not allowed to rotate the unit cell to fill the space, ok.

Now, one of the, one very useful way to visualize unit cell is that you imagine that the this unit cell that you have a some solid object and you want to stack up these solid objects, in 3D space, stacked them up in all directions and see if they fill the entire space, ok.

Now, the other point I want to make is that because of this condition that the unit cell should fill the entire space, you can see that such a triangle cannot be a choice of a unit cell; you cannot have a unit cell in 2D that has this sort of right angle triangle, ok. And actually, this greatly restricts the choice of unit cells, ok. So, this greatly restricts the available shapes of unit cells.

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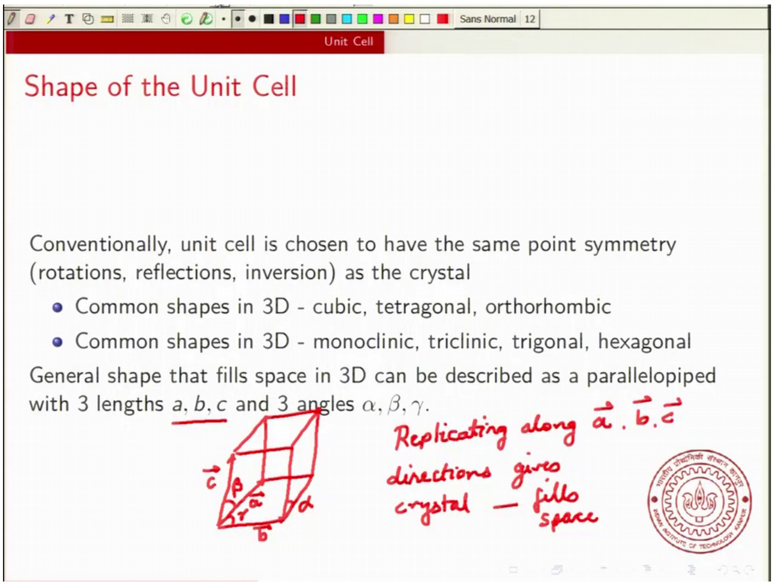

So, now, let us come to the shape of the unit cell, ok. Now, as we said that we have many choices of unit cells, ok. So, conventionally the unit cell is chosen to have a shape that matches that of the entire crystal, ok. So, we will discuss about crystal symmetry later, but basically the unit cell is chosen to have the same point symmetry that means, in terms of rotations, reflections and inversions as the as the crystal itself, ok. So, the crystal has certain symmetries, and the unit cell is chosen to have the same symmetries and this will become clear as we learn more about crystals, ok.

Now, the common shapes in 3D you can have cubic, tetragonal, orthorhombic, triclinic, monoclinic, trigonal or hexagonal, ok. And we can understand all these in terms of in terms of in terms of what we said it just now, that we imagine that unit cell to be some solid object that fills the entire space, ok. Now, if we look at the general kind of solid object in 3D that fills the entire space, such an object would be a parallelepiped, ok. So, and I will just show you what this parallelepiped will look like. So, it will have, it will have sides, that I will show by; so, you take you take 3 vectors a, b and c, and you construct a parallelepiped using these 3 vectors, ok. So, what I did was I took 3 vectors, a, b and c and I constructed a parallelepiped using these 3 vectors, ok. And let me put a vector arrow on each on each of a, b and c, ok.

So, a typical unit cell will have such will have such character, such characteristics it will look like a parallelepiped a general unit cell and so now, there are 3 vectors, which have lengths a, b and c, and there are angles between the vectors. So, the angle between a and b I will call it as gamma, the angle between a and c I will call it as beta and the angle between c and b, let me show it here, just so that you do not get confused between c and b I will call this as alpha, ok. So, there are 3 angles alpha, beta gamma, which are also used to specify the unit cell.

So, if you take this parallelepiped and you extend it along these along the along the a, b and c directions. So, extending or I should I should use a word replicating, so you repeat this parallelepiped. So, replicating along a, b, c directions gives crystal or essentially it fills space, and it fills space, ok.

Now, so, well you say that if you have a parallelepiped with these lengths a, b, c and angles alpha, beta, gamma, well you have many shapes, ok. You have it seems that you have a very large number of possible shape, ok, you can choose each of them arbitrarily and you can you can hope to you can imagine that it might fill space. Now, it turns out that that yes, you can you can do this, but there are still certain restrictions and I will discuss that in the in the next; I will discuss that right now.

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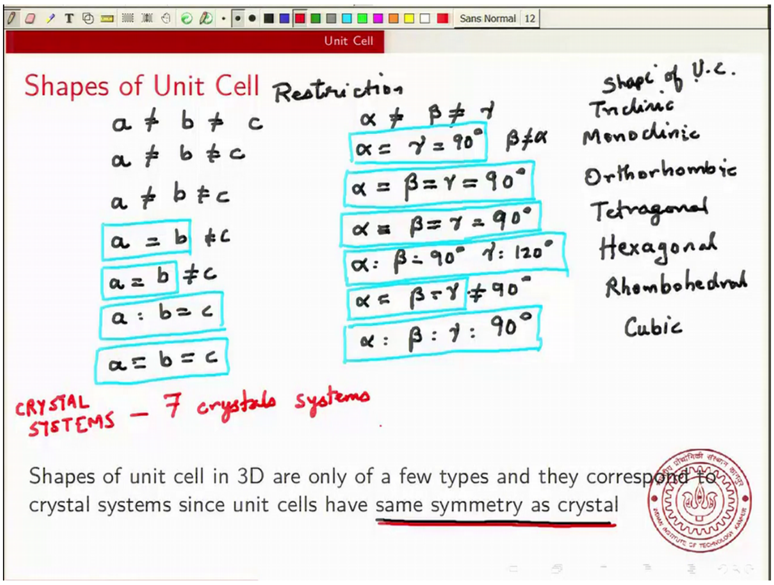

So, the shapes of the unit cell can be can be understood in terms of these of this parallelepiped. So, we have a, b c and you have alpha, beta, gamma, ok. Now, suppose I say that a is not equal to b, and a, b and c are all different from each other. So, a is not equal to b, b is not equal to c and c is not equal to a similarly alpha, beta, gamma are different from each other. This is the most general cell, and basically there is no restriction, ok. So, there is no restriction, ok. So, let me call this as the restriction, ok.

Now, on the other hand you could have something like this, a you could have a restriction that a is not equal to b not equal to c, but let us say alpha equal to gamma equal to 90 degrees and beta is not equal to alpha, ok. So, now, such a restriction, it this restriction on the unit cell, you should it basically says that you know you know there are only certain cells that can have this sort of restriction, ok. Now, well I should I should say its slightly differently let me let me say this is no restriction. So, here there is no restriction on a, b and c, similarly there is no restriction on alpha beta gamma here there is a restriction, ok.

So, let me underline the restriction. So, alpha equal to gamma equal to 90 is the actual restriction, ok. So, we are saying that a, b, c can be completely independent of each other, but alpha equal to gamma equal to 90 degree is the restriction, ok. So, I am just putting the restriction in a square box, ok.

And you can go ahead you can make more restrictions and you can see, we can see, let me just write, ok. So, the case, not equal to b not equal to c, alpha equal to beta to gamma equal to 90 degrees. So, now the restriction here is that alpha equal to beta equal to gamma equal to 90 degrees, ok. Let me emphasize in the first case is actually no restriction, second case there is a restriction, you cannot have alpha beta gamma be arbitrary, ok. And now, and in the third case I said I said alpha should actually be equal to beta and that should be equal to gamma and it all of them should be 90 degrees, ok.

You can have more restrictions, you can have a restriction where whether it is a is equal to b. So, the restriction now is that a is equal to b, and let me let me write for completeness that it is not equal to c, ok. Just to emphasize the cell, ok. And you still have let us say alpha equal to beta equal to gamma and alpha equal to beta equal to gamma and this is not equal to 90 degrees, ok. Now, let me emphasize again that when I write not equal to, that is not really a restriction, ok. So, the restrictions here are a equal to b and alpha equal to beta equal to gamma.

Now, the next kind of cell that I am thinking of is where you have a equal to b not equal to c and alpha equal to beta equal to 90 degrees and gamma equal to 120 degrees. Now, I have many more restrictions. So, not only are a do a and b have to be equal to each other, but you have all these restrictions alpha be; alpha has to be equal to 90 degrees, beta has to be 90 degrees and gamma has to be 120 degrees. And then let me take a couple of more a, more things. So, if you take a equal to b equal to c and alpha equal to beta equal to gamma and this will say it is not equal to 90 degrees. So, here the restriction is that a, b and c have to be identical, and alpha, beta and gamma have to be identical, ok.

And finally, the one with the most strict restrictions is when a equal to b equal to c and alpha equal to beta equal to gamma equal to 90 degrees, ok. So, this is the in some sense everything is restricted. So, a, b, c are identical and alpha beta gamma are identical and they are 90 degrees. So, you can see that as we go down we are putting more restrictions on the cell, ok. And if a cell if you have a unit cell that satisfies this, it is such a unit cell is called a cubic unit cell. Then this unit cell, ok, so this is the shape of the unit cell. So, I will just call the shape of put the shape of the unit cell here, ok. So, the shape, this shape is referred to as a rhombohedral shape, ok

Now, let me emphasize one more thing that this is the shape of the unit cell, this is the shape of unit cell, it is not these are the shapes of the unit cell, ok. Now, let us look at the other restrictions, ok. So, then this shape is called refers to hexagonal unit cell. I will discuss this a little bit later in the course. This shape refers to this is actually it should make a small correction, ok. So, this is actually should be equal to 90 degrees, ok. So, this is actually the restriction that this should be equal to 90 degrees, alpha, equal to beta equal to gamma equal to 90 degrees. This refers to a tetragonal cell this refers to orthorhombic, this refers to monoclinic and this refers to triclinic, ok.

So, basically a triclinic cell has no restriction and what is important is that for a triclinic cell a is not equal to b not equal to c and alpha is not equal to beta not equal to gamma, ok. Now, if you take a monoclinic cell, ok. So, that has a restriction that alpha and gamma should be 90 degrees, ok. And now if you find that a crystal satisfies this restriction that alpha equal to gamma equal to 90 degrees, then you can say that it I mean because the triclinic is has no restrictions so it could be either monoclinic or triclinic, ok. If it satisfies several other restrictions, then it could be one of these, ok.

Now, again this just refers to the shape of the unit cell when these conditions are satisfied, ok. And what is interesting is that there are only a few types of shapes of unit cells, ok. So, we see that there are only few types of shapes of unit cell and therefore, we realize that there are only a few types of crystals, ok. So, because we said that the unit cell should have the same symmetry as a crystal, so there are only a few types of crystals, ok. And actually, we will see that there are these things that we learn later called crystal systems, and actually there are only 7 crystal systems. So, all crystals can be classified into these 7 crystal systems, ok.

Now, usually you cannot I mean the crystal systems will also have names like triclinic, monoclinic, orthorhombic, tetragonal, hexagonal and instead of rhombohedral they the crystal system is actually trigonal, trigonal crystal system and then there is cubic crystal system. So, these are the 7 crystal systems, ok. Now, it is not, you cannot say that if you know I mean the seven crystal systems, they might have different unit cell shapes also, ok. So, you cannot look at the unit cell shape and can say what the crystal system is, ok.

So, in the next class I will look we will look more in detail about unit cell, ok. We look at different kinds of unit cells both the primitive and conventional unit cells, and then I will start talking about lattices, ok.

Thank you.